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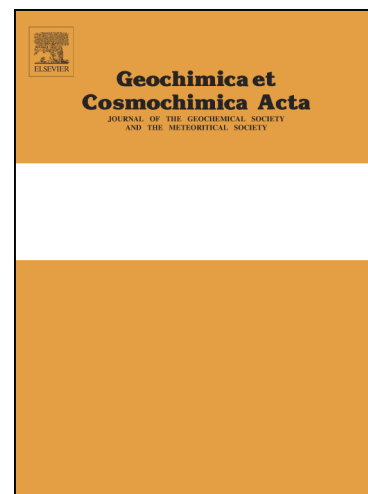
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## Water in evolved lunar rocks: Evidence for multiple reservoirs

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## Water in evolved lunar rocks: Evidence for Multiple Reservoirs

### Abstract

We have measured the abundance and isotopic composition of water in apatites from several lunar rocks representing Potassium (K), Rare Earth Elements (REE), and Phosphorus (P) - KREEP - rich lithologies, including felsites, quartz monzodiorites (QMDs), a troctolite, and alkali anorthosite. The H-isotope data from apatite provide evidence for multiple reservoirs in the lunar interior. Apatite measurements from some KREEP-rich intrusive rocks display moderately elevated  $\delta D$  signatures, while other samples show  $\delta D$  signatures similar to the range known for the terrestrial upper mantle. Apatite grains in Apollo 15 quartz monzodiorites have the lowest  $\delta D$  values measured from the Moon so far (as low as - 749 ‰), and could potentially represent a D-depleted reservoir in the lunar interior that had not been identified until now. Apatite in all of these intrusive rocks contains < 267 ppm  $H_2O$ , which is relatively low compared to apatites from the majority of studied mare basalts (200 to > 6500 ppm  $H_2O$ ). Complexities in partitioning of volatiles into apatite make this comparison uncertain, but measurements of residual glass in KREEP basalt fragments in breccia 15358 independently show that the KREEP basaltic magmas were low in water. The source of 15358 contained ~ 10 ppm  $H_2O$ , about an order of magnitude lower than the source of the Apollo 17 pyroclastic glass beads, suggesting potential variations in the distribution of water in the lunar interior.

### 1. Introduction.

The detection of water in lunar volcanic glasses, apatites, and melt inclusions has implications for planetary accretion, the source(s) of water in the Earth-Moon system, and the role of water in lunar evolution (Saal et al., 2008; McCubbin et al., 2010; Boyce et al., 2010; Greenwood et al., 2011; Hauri et al., 2011; Tartèse et al., 2013, 2014; Barnes et al., 2013, 2014a). (In this paper we use “water” as a shorthand way of referring to all hydrogen species,  $H_2O$ , OH, and  $H_2$ . More than one may be present, depending on oxygen fugacity and pressure (e.g., Hirschmann et al., 2012.) Recent work has shown that apatites in mare basalts contain appreciable amounts of water, and are generally enriched in deuterium ( $^2H$ , or D) with respect

to Earth, possibly due to the addition of D-rich material early in the Moon's history (Greenwood et al., 2011) or to the loss of H preferentially over D during magma degassing (e.g. Saal et al. 2008; Tartèse and Anand, 2013; Tartèse et al., 2013, Saal et al., 2013). The final fraction of the global lunar magma ocean (LMO) model is considered to be urKREEP, so named for its enrichment in incompatible elements compared to other lunar materials (e.g., Warren and Wasson, 1979). Because water behaves as an incompatible element in major silicate phases that formed during the LMO crystallization (Koga et al., 2003; Aubaud et al., 2004; Grant et al. 2007), KREEP-rich rocks are expected to be enriched in water relative to other lunar rocks. Many KREEP-rich lithologies consist of evolved rocks that formed as intrusions, which means that they would have avoided or experienced minimal water loss (unlike the mare basalts), and potential hydrogen isotope fractionation due to magmatic degassing.

The mineral apatite  $[\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})]$  incorporates OH into its crystal structure, making it a potential recorder of the concentration of OH in magma at the time of apatite crystallization. The OH in apatite is resistant to exchanging O or H with adsorbed terrestrial water on thin section surfaces (Greenwood et al., 2011) hence it is useful for H isotopic measurements by secondary ion mass spectrometry (SIMS). The D/H ratio, expressed as  $\delta\text{D}$  (‰)  $= ([\text{D}/\text{H}]_{\text{sample}}/[\text{D}/\text{H}]_{\text{standard}} - 1) \times 1000$ , relative to Vienna Standard Mean Ocean Water (V-SMOW), is important for identifying the source of the Moon's water and the extent of water loss during magmatic processing (e.g., Greenwood et al., 2011; Elkins-Tanton and Grove, 2011; Tartèse et al., 2013). Previous studies have demonstrated that the water content of lunar apatite varies among different rock types. Apatites in Apollo mare basalts record the highest  $\text{H}_2\text{O}$  contents (up to ~7500 ppm) and  $\delta\text{D}$  (+390 to +1100‰) (McCubbin et al., 2010; Greenwood et al., 2011; Barnes et al., 2013; Tartèse et al., 2013), while apatites in more evolved, KREEP-related rocks generally have lower  $\text{H}_2\text{O}$  contents (< 3000 ppm) and  $\delta\text{D}$  values (-384 to +791‰, Greenwood et al., 2011; Barnes et al., 2014a; Tartèse et al., 2014; Robinson et al., 2013, Robinson and Taylor, 2014).

Though it was initially thought that apatite water contents could be used to infer initial magmatic water abundances (McCubbin et al., 2010, Boyce et al., 2010, Tartèse et al., 2013,

2014, Barnes et al. 2014a), Boyce et al. (2014) demonstrated that the F-Cl-OH partitioning into apatite is not well-described by a simple apatite-melt partition coefficient. Apatite water content thus cannot be used to quantitatively determine the amount of water in the co-existing melt, unless the F or Cl content are also known for both melt and apatite, and that it can be confirmed that apatite crystallized in equilibrium with the melt. However, the measured D/H ratios are still useful for gaining insights into processes that might have affected the parental magmas.

Rocks formed in an intrusive environment could have experienced minimal D-H fractionation and water loss prior to apatite crystallization because they form at pressures where water is far more soluble in silicate melt than at low pressures near or on the surface (e.g., Dixon et al., 1995). Water solubility in magmas decreases with decreasing pressure, so when a hydrous magma approaches a planetary surface, the melt degasses and water is lost assuming water is present as OH and H<sub>2</sub>O. Diffusion modelling of water loss from volcanic lunar pyroclastic glasses indicates that they lost up to 98% of their initial water content upon eruption (Saal et al., 2008). Mare basaltic magmas would also have degassed during eruption onto the lunar surface, but probably less than the 98% loss experienced by pyroclastic glasses. Based on water contents of melt inclusions in olivine from subaerial and submarine Hawaiian lavas (which have little water loss due to the pressure at which they erupted; Hauri 2002), we estimate that lava flows lose up to 90% of their pre-eruptive H<sub>2</sub>O. Low-Ti mare magmas could have lost 85 to 99% of their pre-eruptive water contents (Tartèse et al., 2013), but such estimates assume an initial D/H ratio. The degassing of hydrogen from a magma or lava also fractionates lighter H from heavier D, especially if H<sub>2</sub> is lost rather than H<sub>2</sub>O (e.g. Richet et al., 1977; Tartèse and Anand 2013; Tartèse et al., 2013). Degassing experiments with apatite suggest that volatile loss occurs rapidly in extrusive magmas, and that apatite, which forms late, will not preserve pre-eruption volatile contents and will instead reflect the post-degassing volatile composition of the magma (Ustunisik et al., 2015). The erupted mare basalts have the highest  $\delta D$  values (up to  $\sim +1100\text{‰}$ ) found in lunar rocks so far (Greenwood et al., 2011; Barnes et al., 2013; Tartèse et al., 2013).

Apatite in intrusive rocks may represent a more pristine sampling of the lunar interior water than the water bound in apatites in the mare basalts, due to their formation at depth at higher pressures (Robinson et al., 2013; Robinson and Taylor, 2014; Barnes et al., 2014a). Reaction relations in symplectitic intergrowths in troctolite 76535 indicate a depth of origin of ~40 km (Gooley et al., 1974; McCallum et al., 2006), corresponding to a pressure of over 1.5 kb. On the other hand, gabbro-norite sample 76255 may have formed as shallow as a few kilometers (McCallum et al., 2006), and quartz-monzodiorite 14161, 7373 as shallow as 1 km (Jolliff et al., 1999), at a pressure of 50 b. The liquidus temperatures and presence of quartz in highly fractionated lunar felsites (Hess et al., 1975; Hess et al. 1978; Hess et al. 1989; Robinson and Taylor, 2011; Robinson et al., 2015) indicate crystallization at a pressure of at least ~1 kb (Tuttle and Bowen, 1958), corresponding to a depth of over 20 km, assuming a crustal density of 2550 kg/m<sup>3</sup> (Wieczorek et al., 2013). Up to 3 wt. % H<sub>2</sub>O is soluble in rhyolitic melts at ~1kb, and even 0.5 wt.% would have been soluble at the 50 b pressure experienced by the parental melt for QMD 14161, 7373 (VolatileCalc, Newman and Lowenstern 2002; Jolliff et al. 1999). Common mineral phases associated with hydrous melts such as amphibole and micas have never been reported in lunar rocks, and no lunar magma has been shown to have contained weight percent levels of water (e.g. Robinson and Taylor, 2014 and references therein). While the concentration of water in the melt would have increased during crystallization, it would have had to reach weight percent levels to degas *before* apatite crystallization began and removed F, Cl, and OH from the melt (Boyce et al., 2014). Assuming that water is completely incompatible in the crystallizing silicates and that a magma had an initial H<sub>2</sub>O content of 0.1 wt% (similar to A17 melt inclusions, Saal et al., 2013), the H<sub>2</sub>O concentration would have only increased to 1 wt.% after 90% crystallization. Apatite forms after 90% crystallization in basaltic systems, and earlier in KREEP-rich melts (Harrison and Watson, 1984; Tartèse and Anand, 2013; Tartèse et al. 2014). Unless they were exceptionally water-rich, water would have remained soluble in the parental melts for all the KREEP-rich intrusive rocks discussed here.

While H loss by degassing may not occur in the KREEP-rich intrusive rocks, their H isotopes could be affected by diffusion. Studies of melt inclusions in basalts show that lighter H can escape from melt inclusions by diffusion, therefore enriching heavier D in the melt inclusion

over time (Gaetani et al., 2012, Bucholz et al., 2013). It is unclear if a similar process affected the H isotopes in apatite from the KREEP-rich intrusive rocks, or if H from country rock surrounding the magma bodies could have been incorporated. However, in order for H to be lost (or gained), it would have to diffuse through either a liquid or solid medium. This would have a less extreme fractionation effect than degassing into vacuum or a low-pressure environment (Bucholz et al., 2013). A magmatic system is more complex than a melt inclusion, and some water loss and H isotope fractionation might occur, but apatite in a rock formed intrusively is generally more likely to have retained the isotopic composition of lunar interior water than rapidly degassed samples such as apatite in mare basalts or glass in pyroclastics.

If water was present in the lunar magma ocean, it should be highly concentrated in KREEP-rich materials, assuming no significant loss occurred during magma ocean crystallization and subsequent cumulate overturn (Tartèse et al., 2014). Anything KREEP-rich or derived from KREEP basaltic magmas should also be enriched in water. However, it is not a simple path from late-stage magma ocean products to KREEP-rich or KREEP-related magmas, which formed either by the assimilation of the urKREEP component by rising Mg-rich diapirs at the base of the lunar crust, or by the partial melting of hybrid mantle sources, formed by sinking urKREEP (and other dense components) mixing with Mg-rich olivine-orthopyroxene cumulates (Shearer and Floss, 1999; Shearer and Papike, 2005; Elardo et al., 2011). Regardless of the formation mechanism, these magmas gave rise to what we now know as the KREEP basalts, and the norites and troctolites of the magnesian (Mg) suite (recently reviewed by Shearer et al., 2015). Fractional crystallization of magmas resembling KREEP basalts is thought to have produced geochemically evolved rocks such as quartz monzodiorites (Ryder, 1976; Ryder and Martinez, 1991, Jolliff 1991). Alternatively, silicate liquid immiscibility (SLI) is proposed to have played a role in the formation of the lunar felsites (e.g., Hess et al., 1975, Warner et al., 1978 Snyder et al., 1995; Ryder and Martinez, 1991, Shearer et al., 2015). Most importantly, any petrologic processing took place inside the Moon at pressures high enough to inhibit water loss from magmas or mantle rocks.



## 2. Samples.

The felsites and quartz monzodiorites (QMDs) are both intrusive late-stage fractionates of KREEP-basaltic magmas (Ryder et al., 1975; Ryder and Martinez, 1991). The felsite suite consists of evolved Si-rich (~ 70 wt % SiO<sub>2</sub>) rocks with graphic intergrowths of quartz and K-feldspar (Ryder et al., 1975; Warner et al., 1978; Taylor et al., 1980; Warren et al., 1983, 1987; Jolliff 1991; Robinson and Taylor, 2011). Silica-rich compositions can be generated by partial melting, but extensive fractional crystallization also produces silica-rich melt through the process of silicate liquid immiscibility (SLI) (e.g. Rutherford et al., 1974). After 90-98% crystallization of a basaltic magma, the remaining liquid will spontaneously separate into Si-rich and Fe-rich liquids (FeO 12-14 wt. %; Roedder and Weiblen 1971, Hess et al. 1975). The Si-rich end member is called a felsite, while the Fe-rich end member is called a ferrobalt (Rutherford et al., 1974). Based on felsite texture and the presence of quartz, rather than another silica polymorph, the felsites and their corresponding Fe-rich phases formed in small intrusive bodies through silicate liquid immiscibility of an evolving magma of KREEP-basalt composition (e.g. Warner et al., 1978; Taylor et al., 1980; Warren et al., 1983; Robinson and Taylor 2011).

Felsite sample 14321,1047 is well-known, consisting of clasts of graphically-intergrown quartz and K-feldspar, and resides in clast-rich impact breccia 14321 (Warren et al., 1983; Fig. 1a). Apatite was found enclosed by quartz in Si-rich 14321,1047, suggesting that it was a liquidus phase. Sample 77538,16 is unique in that it preserves both silicate liquid immiscibility end-members in co-existing felsite and ferrobalt areas (Warner et al. 1978)(Fig. 1b). Apatite was found in both the Si-rich and Fe-rich end members; it is enclosed in clinopyroxene in the Fe-rich regions of 77538 and in K-feldspar in the Si-rich regions of 77538.

The quartz monzodiorites (QMDs) are also evolved rocks. They exhibit a cumulate texture and are probably fractional crystallization products of KREEP basaltic magmas (Ryder and Martinez, 1991; Jolliff 1991), though not quite as extreme fractionates as the felsites. Many contain exsolved pyroxenes, indicating they formed in a slow-cooling, intrusive environment. Both 14161,7069 (Fig. 1d) and -,7373 were classified as QMDs (Jolliff 1991). Section 14161,7373 is particularly notable for its inverted, exsolved pyroxenes and high phosphate

content, mostly in the form of whitlockite (Jolliff 1991); strictly speaking, this anhydrous phosphate is more properly called merrillite (Hughes et al., 2006; Jolliff et al., 2006; Hughes et al., 2008; McCubbin et al., 2014). Based on An contents of plagioclase some QMDs are probably more accurately described as monzogabbros, but we use monzodiorites here to maintain consistency with the majority of previously published literature on these samples.

We studied three QMD clasts from soil sample 15400, (15404,51, 15404,55 and 15403,71) which was likely derived from the top of a large boulder (sampled as 15405) at Station 6A on the Apollo 15 mission. Sample 15403,71 is a single fragment from the 2-4 mm fraction of 15400. It consists of roughly 50% impact melt and 50% shocked QMD. The QMD contains large phosphates, including a single > 500  $\mu\text{m}$  apatite grain (Marvin et al., 1991). Sample 15404,51 and ,55 come from the 4-10 mm size fraction. Apatite in QMD 15404,51 was studied previously by McCubbin et al. (2010). Sample 15404,55 (Fig. 1c) is also a QMD, from the same chip and lithology as 15404,51. In each of the three thin-sections studied, pyroxene shows fine exsolution lamellae, indicating an intrusive origin. Moreover, the samples' enrichment in rare earth elements (Lindstrom et al., 1992), relative to Apollo 15 KREEP basalts, show they probably formed via fractional crystallization of an Apollo 15 KREEP-like magma, as shown by previous studies (e.g., Ryder and Martinez, 1991; Taylor et al., 2012).

Alkali anorthosite clasts were studied in breccia 14305,656 (Fig.1f). The alkali anorthosites are also products of fractional crystallization of a KREEP-rich basaltic magma, thought to have formed as flotation cumulates in intrusive magma bodies (Shervais and McGee, 1999). Merrillite was reported in other alkali anorthosite sections of 14305 (Shervais and McGee, 1999), and our thin-section seems to be particularly rich in merrillite. Apatite is intergrown with merrillite in sample 14305,656.

Troctolite 76535 is coarse-grained and shows signs of slow subsolidus annealing, leading to the interpretation that it could have formed at depths of tens of kilometers in the crust, significantly inhibiting water loss (Gooley et al., 1974; Dymek et al., 1975; Schwartz and McCallum, 1999). There are also reports that this rock may have been altered by post-crystallization metasomatism, which likely would have altered the magmatic volatile contents

of apatite in this rock (Elardo et al., 2012; Barnes et al., 2014a). We measured apatites in two thin-sections, 76535,52 and -,56 (Fig 1e). The troctolite is not directly derived from KREEP basaltic magma like the felsites or QMDs, but it does have a high-KREEP content as revealed by trace element analyses of mineral grains (Shearer and Floss, 1999).

We also examined two KREEP basalt fragments in impact melt breccia 15358,6. These KREEP basalts have intersertal to intergranular textures and abundant yellow glass that is interpreted to be the last 11-18 % of a KREEP basaltic melt, which quenched instead of crystallizing (Ryder 1988; Taylor et al. 2012). No evidence for the clasts being impact melt breccias, such as unmelted mineral fragments, is present (Taylor et al., 2012). Apatite large enough for SIMS analysis was not identified in either fragment; instead the D/H ratio and H concentration of the glass was measured. These unique clasts likely represent late-stage break outs from KREEP basalt lava flows (Taylor et al., 2012).

### 3. Methods

*3.1. Secondary Ion Mass Spectrometry (SIMS).* Two instruments, the Cameca ims-1280 and the NanoSIMS 50L, have both been successfully used to measure H isotopes in extraterrestrial apatite (e.g. Hallis et al., 2012; Robinson et al., 2012; Barnes et al., 2013; Tartèse et al., 2013; 2014). The ims-1280 has higher analytical precision, but a large analysis size. The 50L NanoSIMS has a smaller analysis size, allowing the measurement of apatites that are too small or cracked to be analyzed with the ims-1280. This paper reports data from both instruments, and the respective protocols are described below.

*3.1.1. University of Hawaii (UH).* The protocol for measuring H isotopes in apatite at UH was developed for use with both Martian and lunar materials. A detailed description of this protocol can be found in Hallis et al. (2012). Lunar apatites were analyzed *in-situ* with the ims 1280 secondary-ion mass spectrometer during four separate analytical sessions (May and November 2011, August 2012, and July 2014). We used a 2 nA Cs<sup>+</sup> primary beam (4 nA in August 2012 and July 2014). The secondary-ion mass spectrometer was operated at 10 keV (giving a 20 keV impact energy) with a 50 eV energy window. The mass resolving power was

~1900 (defined as peak width at 10% of peak height), sufficient to separate any interfering molecular ions. A normal-incidence electron flood gun was used for charge compensation of the analyzed area.

Using a rastered beam, a  $25 \times 25 \mu\text{m}^2$  area was sputtered for 300 s to remove the carbon coat and any surface contaminants before the actual measurement took place. During the pre-sputtering, we monitored the H ion image to identify and then avoid any possible terrestrial contamination. In the H ion image, H-rich material such as epoxy or small cracks appears very bright. The beam was repositioned (when possible), in order to avoid H-rich areas. The measurement was aborted if no “clean” area could be identified.  $^1\text{H}^-$ ,  $^2\text{D}^-$ , and  $^{18}\text{O}^-$  were then measured sequentially on an electron multiplier in monocollection mode from a reduced rastered area of  $15 \times 15 \mu\text{m}^2$ . For glass measurements, ions of  $^{30}\text{Si}^-$ , instead of  $^{18}\text{O}^-$  were collected. An electronic gate was used to exclude counts from all but the inner  $\sim 8 \times 8 \mu\text{m}^2$  of this area to avoid the edges of the sputtered pit and H creep across the sample surface. If contamination appeared (as a very bright signal on the H image and/or a sudden large spike in the H count rate) during the course of a measurement, the affected cycles were eliminated during data reduction.

Each measurement consisted of 40 cycles.  $^1\text{H}$  was counted for 3 s, D for 40 s, and  $^{18}\text{O}$  (or  $^{30}\text{Si}$  for glasses) for 2 s in each cycle. The primary beam was blanked for the first 10 and final 5 cycles in order to measure background H and D signals (mainly contributed by the electron gun). The background counts were subtracted from the measured isotope signal, which was collected between cycles 11 and 35 while the beam was positioned on the sample. We made appropriate corrections in data analysis to account for the electronic gate and deadtime of the electron multiplier (c.f. Hallis et al., 2012). Hydrogen isotopes of KREEP basalt glasses were measured on the same instrument in March 2012 using the same analytical conditions.

The SIMS measurements were calibrated prior to lunar apatite measurements using 3 natural terrestrial apatite standards (Ap003 Durango, Ap018 Russia, and Ap005 Crystal Lode), mounted in epoxy, that were characterized previously by McCubbin et al. (2012). Ap018 and Ap005 were also used for instrumental mass fractionation corrections of measured D/H ratios.

The H<sub>2</sub>O content of lunar apatite was determined from their measured <sup>1</sup>H/<sup>18</sup>O ratios and a calibration curve of H<sub>2</sub>O (wt.%) vs. <sup>1</sup>H/<sup>18</sup>O determined using the 3 apatite standards with different H<sub>2</sub>O abundances (Fig. 2a). The curve was forced through the origin.

For the KREEP glass measurements, we used two basaltic glass standards (D52-5 and D51-3) with published D/H ratios (Hauri et al., 2002). The H<sub>2</sub>O contents of these two standards were determined by Rhea Workman using FTIR at Caltech. The H<sub>2</sub>O content of KREEP glass was calculated using a calibration curve (Fig. 2b) for H<sub>2</sub>O (wt.%) vs. <sup>1</sup>H/<sup>30</sup>Si. That curve was also forced through the origin. The reported errors on water contents and δD values include both the internal precision of an individual analysis and the external reproducibility (standard deviation) for standard measurements during a given analytical session.

The detection limit for H<sub>2</sub>O content was estimated by measuring nominally anhydrous minerals, such as olivine and pyroxene present in the same thin-sections, and a San Carlos olivine standard in a separate, epoxy-free standard mount. Samples were stored in a 60 °C vacuum oven to minimize the adsorption of water on section surfaces. As shown in Table 1, measurements with 2 nA primary beam resulted in a detection limit of ~ 100 ppm. The detection limit was later significantly improved by up to 10x by using a 4 nA primary beam. At least two things conspire to produce this improvement. First, a higher beam current increases the signal from the species that make up the sample, while the H from the vacuum system and that creeping along the sample surface remains approximately constant. Second, a higher beam current could more-efficiently remove surface H creeping in to the measurement area, thereby reducing the contaminant steady-state value. Yurimoto et al. (1989) and Stéphant and Robert (2014) also reported that use of higher primary beam current efficiently improves the detection limit of hydrogen measurement.

*3.1.2 The Open University (OU).* The Cameca NanoSIMS 50L was used for determining the H<sub>2</sub>O contents and H isotopic composition of apatites following the protocol described in details in Barnes et al. (2013, 2014a) and Tartèse et al. (2013). Polished samples were gold-coated for NanoSIMS analysis. A Cs<sup>+</sup> primary beam of ~ 260 pA current was used and negative secondary ions of <sup>1</sup>H, D, <sup>12</sup>C, and <sup>18</sup>O were collected simultaneously on electron multipliers. Electronic

gating was used to restrict counting secondary ions to the innermost 25 % of the sputtered area. Before analysis, pre-sputtering was performed over a 20  $\mu\text{m}$  x 20  $\mu\text{m}$  area using a  $\sim 600$  pA primary beam for 1 minute to clean the sample surface and to locate the apatite using real time imaging (RTI), then further pre-sputtering was performed at a reduced area (analysis area) using the same beam conditions. An electron gun was used to provide charge compensation. Because of the variation in apatite grain size within and between samples, and the need to avoid cracks or inclusions, the analysis areas varied from 8  $\mu\text{m}$  x 8  $\mu\text{m}$  to 5  $\mu\text{m}$  x 5  $\mu\text{m}$ . The vacuum in the analysis chamber during analyses was  $\sim 6.0 \times 10^{-10}$  Torr.

RTI was also carried out during the pre-sputtering to monitor  $^1\text{H}$  and  $^{12}\text{C}$  in order to identify cracks and hotspots. Occasionally, during an analysis a crack or hotspot appeared; in such a case, only the signal corresponding to analysis of the pristine sample was considered. This signal was isolated using the NanoSIMS DataEditor, software developed by Frank Gyngard (Washington University). Data inclusion was based on the  $^{12}\text{C}$  signal, which is very low in lunar apatites but is several orders of magnitude higher for material filling the cracks (c.f. Barnes et al., 2014a; Tartèse et al., 2014).

Three terrestrial apatite standards (Ap003, Ap004, and Ap018 described in McCubbin et al., 2012) pressed in indium were used for calibration along with a “dry” San Carlos olivine crystal. This dry olivine was used to monitor instrumental background, which ranged between 13 and 24 ppm  $\text{H}_2\text{O}$  for the different analytical sessions. To ensure that this measure is adequate for epoxy-mounted samples, analyses were also carried out under routine analytical conditions in two plagioclase crystals in sample 15404. Two analyses of plagioclase yielded between 19 and 33 ppm  $\text{H}_2\text{O}$ , which is considered background  $\text{H}_2\text{O}$  assuming that the crystals are indeed dry. Overall, the calculated background  $\text{H}_2\text{O}$  contents for indium-pressed dry olivine and epoxy-mounted nominally anhydrous plagioclase were similar. Background  $\text{H}_2\text{O}$  was then subtracted from the measured values of the unknown apatites.

### 3.2. Galactic Cosmic Ray Exposure.

Exposure to cosmic rays on the surface of the Moon can produce D and H *in situ*, which can alter the indigenous D/H ratio of lunar materials. Saal et al. (2013), Barnes et al. (2014a), and Robinson and Taylor (2014) demonstrated the importance of correcting for spallogenic D, especially in materials with low H<sub>2</sub>O content. Spallation-produced D will have a proportionally larger effect on the D/H ratio in samples with low water content than in samples with high water content (Saal et al. 2013) and for samples with long cosmic ray exposure ages. Since the apatites and glasses analyzed in this study have very low water contents (< 300 ppm H<sub>2</sub>O), this correction is important.

The measured data were corrected following the procedure of Saal et al. (2013), by determining the amount of spallation-produced D using the D production rate ( $4.6 \times 10^{-11}$  mol/100 Myr, Merlivat et al., 1976) and the cosmic ray exposure (CRE) age of each sample, and then that contribution was subtracted from the measured D abundance for recalculating the D/H ratio. The reported uncertainty includes the uncertainty in the D production rate and the  $2\sigma$  analytical uncertainties. The large uncertainty in the D production rate dominates the error of the corrected  $\delta D$  values ( $\sim 50\%$ , Saal et al. 2013). Unlike Saal et al. (2013), spallogenically produced H is not taken into account, because correcting for H has little effect on the overall D/H ratio. For example, the typical spallation correction for H expressed as H<sub>2</sub>O is only  $\sim 1$  ppm (Saal et al., 2013).

Cosmic ray exposure age data were available for samples 14321 (23.8 Ma, Lugmair and Marti, 1972; and 24 Ma, Burnett et al., 1972), 14161 (363 Ma, Kirsten et al., 1972), 76535 (195 Ma, Bogard et al., 1975; 211 Ma, Crozaz et al., 1974; 233 Ma, Lugmair et al., 1976). When multiple ages were available, we averaged the ages. Since the error associated with the correction for cosmogenic D is dominated by the large uncertainty on the D production rate, we did not factor errors on the cosmic ray exposure ages into the total uncertainty of the corrected values. As the cosmic ray exposure (CRE) age of sample 15403/15404 has not been determined, the CRE age of  $11 \pm 1.1$  Ma for sample 15405 was used. Soil sample 15400 was collected from on top of 15405, and is classified as an immature soil.



Two samples, 77538 and 15358, have no CRE ages available. Sample 77538 was collected at Station 7 as a rake sample with lunar soil that was designated mature (Meyer, 2015). According to Morris (1978), it takes 100 Ma of exposure time to develop a mature soil. Therefore, we take 100 Ma as the exposure age of 77538 for the purposes of spallogenic D correction, but this is only meant to be a rough estimate. Likewise, 15358 was collected as a rake sample from the rim of Spur Crater. Another KREEP basalt from the same rake sample, 15382, has been CRE dated to 230 Ma (Stettler et al., 1973) and 240 Ma (Turner et al., 1973). We use the average of these two dates as an estimate for the CRE age of 15358.

#### 4. Results

Although we measure H, we report its concentration as H<sub>2</sub>O equivalent. In the lunar literature, “water” has been used to describe the presence of H, OH, or H<sub>2</sub>O collectively. As explained by Robinson and Taylor (2014), in magma “water” is present largely as OH until the total concentration reaches ~3.5 wt.%, at which point H<sub>2</sub>O becomes the dominant molecular species (Dixon et al., 1995). No lunar magmatic water concentrations reach such high levels, implying that it is present dominantly as OH. However, under the reducing conditions (e.g., IW-1) prevailing in lunar magmas, “water” probably consists of a combination of OH and H, with the proportion of H rising with increasing P and decreasing fO<sub>2</sub> (Elkins-Tanton and Grove, 2011; Hirschman et al., 2012, Sharp et al., 2013). To avoid confusion because of the uncertainty in how much of each species is present, we report our results as H<sub>2</sub>O equivalent. This approach is similar to reporting total Fe as FeO in electron microprobe analyses.

We performed analyses with the UH ims-1280 on a total of 18 points among 11 apatite grains from eight thin sections of intrusive rocks to determine their D/H ratios and water contents. We also made four measurements of residual glass in two KREEP basalt clasts in sample 15358,6 using the same instrument. Many apatite grains are too small (<30 μm) or too cracked to be measured with the ims-1280, so they were analyzed with the NanoSIMS 50L ion microprobe at the Open University. A total of 19 points among 13 apatite grains from three thin sections were measured using the NanoSIMS. All of the δD values, water contents, and



their associated uncertainties are listed in Table 1. Apatite data are plotted on Fig. 3 and compared with literature apatite data in Fig. 4. Some of the data obtained with the ims-1280 was first reported in Robinson et al. (2012, 2013) and Robinson and Taylor (2014).

The low H<sub>2</sub>O contents measured in KREEP-related materials (ranging from 23-267 ppm) is in stark contrast to apatite in most mare basalts, which contain ~1000-7500 ppm H<sub>2</sub>O (Fig. 4). One apatite in felsite 14321,1047 and two apatites in QMD 14161,7373 had H<sub>2</sub>O content below our detection limits. The KREEP basalt residual glass was similarly found to be water-poor, containing 58-95 ppm H<sub>2</sub>O with elevated  $\delta D$  value of +610 to +830 ‰ (Table 1).

The range in  $\delta D$  values for apatite in intrusive samples measured here is astoundingly large, varying from ultralow (-749 ‰) to quite elevated (+973 ‰). There are substantial uncertainties on the NanoSIMS measurements ( $2\sigma$  from 317-650‰) due to poor counting statistics when using relatively low probe currents, which are a result of low water abundances in the apatite, but these data are consistent with more precise measurements of apatite in the same sample (14321,1047 apt1) made with the ims-1280. Correction for spallogenic D decreases the  $\delta D$  value by up to 184‰, yet many lunar apatites with detectable water show  $\delta D$  values higher than in the Earth's mantle, -218 to +60‰ (Boettcher et al., 1980; Michael 1998; Ahrens 1989; Deloule et al., 1991; Bell and Rossman 1992; Thompson 1992; Graham et al., 1994; Jambon 1994; Wagner et al., 1996; Xia et al., 2002; Hallis et al., 2015). The  $\delta D$  values of other apatites fall near or somewhat below the terrestrial range. However, the  $\delta D$  of apatite in 15403,71 (as low as  $-749 \pm 56\text{‰}$ ) is by far the lightest  $\delta D$  value yet reported from the Moon, indicating that there could be a low D source in the lunar interior.

## 5. Discussion.

The data reported here and those previously published suggest that hydrogen isotopic compositions and possibly water concentrations vary widely in the lunar interior. Here we evaluate the extent of these apparent heterogeneities and the important implications these can have with regards to lunar formation and differentiation, and the accretion of volatiles to the lunar interior.

## 5.1 Hydrogen isotopic composition: Multiple Reservoirs

Apatites in this sample suite vary widely in  $\delta D$  value (Table 1, Fig. 3, 4), ranging from  $-754 \pm 57 \text{ ‰}$  to  $+934 \pm 514 \text{ ‰}$  (spallation corrected). The  $\delta D$  values of apatites in individual samples (measured in this study and also in the literature) can also vary by 100s ‰ (Fig. 4). To evaluate broad variations among  $\delta D$  values and  $H_2O$  content of many samples, we made a histogram of the lowest D apatite analyses from each sample (Fig. 6). If degassing affected the H isotopic composition of a given sample, the lowest  $\delta D$  value will represent the least degassed  $\delta D$  for that sample. The data seem to cluster into groups with similar  $\delta D$  values. These clusters could represent different reservoirs in the lunar interior, which we evaluate below (Fig. 6).

### 5.1.1. Earth-like reservoir.

The range in  $\delta D$  value of Earth's present day upper mantle is estimated to be between  $-218$  and  $+60 \text{ ‰}$  (Boettcher et al. 1980; Michael 1998; Ahrens 1989; Deloule et al. 1991; Bell and Rossman 1992; Thompson 1992; Graham et al. 1994; Jambon 1994; Wagner et al. 1996; Xia et al. 2002; Hallis et al., 2015), shown by a line on Fig. 6. Several samples, including two KREEP basalts, five KREEP-rich intrusive rocks, and a mare basalt, fall in or near to this range in  $\delta D$  values. As explained above, these KREEP-rich intrusive rocks formed at depth and pressure, so are less likely to have degassed and fractionated D from H prior to apatite crystallization. The rocks could thus retain their original (or close to their original) D/H ratios, which are essentially Earth-like (Barnes et al., 2014a). All of this evidence indicates that there is at least one reservoir in the lunar interior that has a  $\delta D$  value like the terrestrial mantle.

Despite the elevated  $\delta D$  values observed in mare basalt apatites, the mare basalt source may also be similar to the Earth-like  $\delta D$  reservoir. Calculations by Tartèse and Anand (2013) and Tartèse et al. (2013) showed that the entire range of elevated  $\delta D$  values observed in mare basalt apatite could be produced by degassing of 85-99% of the hydrogen from a melt with CI/CM-like chondritic  $\delta D$  signature of  $\sim +100 \text{ ‰}$ , (Alexander et al. 2012). While the water content of the mare basalts appears to be greater than the KREEPy intrusive rocks, they all could have had similar initial  $\delta D$  values, which are in or near the range of the terrestrial mantle.

Saal et al. (2013) and Füri et al. (2014) show that  $\delta D$  values of the pyroclastic glasses can be reconciled (after accounting for degassing) with being derived from a source region in the lunar interior with a  $\delta D$  value in the range of terrestrial rocks and carbonaceous chondrites. This is consistent with the isotopic compositions of olivine-hosted melt inclusions trapped within glass beads (Saal et al., 2013)

#### 5.1.2. Moderately elevated D reservoir.

Another cluster of analyses on Fig. 6 appears between  $\sim 150$ - $350$  ‰. Three of these samples are alkali suite rocks, formed intrusively through extensive fractional crystallization of KREEP basaltic magmas (Snyder et al., 1995). The alkali and Mg-suite rocks, however, formed intrusively and thus did not degas, or degassed little compared to eruptive samples. They could represent a reservoir inside the Moon with an inherent moderately elevated  $\delta D$  signature. It is also possible that these samples represent the high part of a range that begins with the terrestrial values, similar to those ( $\delta D +187$  to  $+327$  ‰) measured in melt inclusions by Saal et al., (2013), and so may not actually be resolvable from the Earth-like reservoir.

#### 5.1.3. Low D reservoir.

A distinct reservoir, with very low  $\delta D$  signature, is represented by apatites from samples 15404,51, and -,55, and 15403,71. Apatite in these samples has an average  $\delta D$  value of  $-630$  ‰, which is far below the range of the terrestrial mantle and of other  $\delta D$  values for apatites reported from the Moon (Fig. 4). REE abundances in 15404,36 (the parent chip of 15404,51 and -,55) are elevated with respect to those of Apollo 15 KREEP basalt (Lindstrom et al., 1992), which is consistent with formation from a KREEP basaltic magma, and its texture (exsolved pyroxene) indicates that it formed intrusively, thus avoiding H fractionation due to degassing. Even if the source of these Apollo 15 QMDs had degassed, degassing elevates  $\delta D$  values, which means that their source would have had an even lower initial  $\delta D$  value.

Solar wind is also extremely depleted in D ( $< -998$ ‰; Huss et al., 2012) and the range in  $\delta D$  values of agglutinate glasses affected by solar wind from the regolith (Liu et al. 2012) is strikingly similar to the range seen in apatites from the Apollo 15 QMDs. However, there is no

clear mechanism for introducing solar wind H into fragments of intrusive rocks residing inside an impact melt. The Apollo 15 QMDs are considered to have formed at depth, in a shallow intrusion in the lunar crust (Ryder and Martinez, 1991), much deeper than D-depleted solar wind could have penetrated. Rock 15405, on which the 15403/4 regolith developed, is an impact melt breccia deposited at the site ca. 1.3 Ga ago. This boulder was probably formed and thrown to the Apollo 15 site by the impact event that formed Aristillus crater (Ryder 1976; Ryder and Martinez, 1991; Ryder et al., 1991; Taylor et al., 2012). It was subsequently buried and brought to the lunar surface at the Apollo 15 site only 11 Ma ago, based on its cosmic ray exposure age (Drozdz et al., 1976). Direct implantation of solar wind H into these apatite grains is unlikely, as solar wind has been demonstrated to penetrate  $< 1 \mu\text{m}$  depth into the surface of a grain. Even if an apatite crystal was exposed directly on the surface the ambient lunar surface temperatures ( $\sim 100^\circ \text{C}$ ) are too low to allow significant diffusion of H into the crystal. Using data from Cherniak (2010) and the interdiffusion coefficient for OH, F, and Cl, the total diffusion distance is only  $\sim 10^{-5}$  microns at  $100^\circ \text{C}$  in 11 Ma.

In order for apatite in the Apollo 15 QMDs to be contaminated with solar wind, H from solar wind would have had to have been incorporated into their source impact melt breccia and subsequently diffused into the apatite grains. As discussed above, these samples were collected from on top of a three-meter boulder, sampled as 15405 (Meyer, 2015). Drozd et al. (1976) measured Ne, Kr, and Xe isotopes in 15405 and Bernatowicz et al. (1978) measured Ar isotopes in 15405 (matrix and a QMD clast) as part of their Ar-Ar dating. Both papers state that the rock contains no measurable solar wind component. Nevertheless, it is worth investigating whether enough regolith could be incorporated into the 15405 impact melt to impart a low  $\delta\text{D}$  signature on the clasts in the rock.

Is it possible that the 15405 impact melt was contaminated with solar wind during its formation by the Aristillus impact? The pre-Aristillus regolith could have been a few meters thick, having formed between 3.8 Ga (the age of Imbrium) and 1.27 Ga (the age of Aristillus). We use 10 m for these calculations. How much of that 10 m layer would then be incorporated into the melt formed during the impact that produced Aristillus crater? Using equations 7.10.2 in Melosh

(1989) for a 55 km crater and assuming an impact velocity of 17 km/sec, a vertical impact angle, impactor density of 3000 kg/m<sup>3</sup>, and target density of 2500 kg/m<sup>3</sup>, we estimate that the projectile would have a radius of 1 km. The fraction of the impact melt derived from regolith is the regolith volume intersected by the footprint of the impacting projectile (1 km). Therefore, the regolith constitutes a disk 10 meters thick and 1 km in radius, equivalent to a volume of 0.031 km<sup>3</sup>. Dividing this by the total volume of the melt produced, 500 km<sup>3</sup> (using projectile size and velocity noted above, after Grieve and Cintala 1992), gives a regolith fraction of 0.0063%. If the regolith contained 100 ppm H (close to the upper limit measured on Apollo regolith samples, Haskin and Warren, 1991), then the impact melt (assuming uniform mixing) would acquire 0.0063 ppm H. If all of the solar wind H was incorporated into apatite and the apatite abundance was 1% (the amount of normative apatite in KREEP basalt), then the apatite would contain a maximum of 0.6 ppm of solar wind derived H from the regolith atop the Aristillus target. This is equivalent to 5.4 ppm H<sub>2</sub>O, which is only ~4% of the average water content of apatite in 15403, 71. Moreover, any solar wind H incorporated from the regolith would have then had to diffuse through the very rapidly cooling impact melt (Onorato et al., 1976) and rock fragments to eventually reach the apatite. We conclude that the low  $\delta D$  signature is not derived from solar wind contamination, but instead reflects the nature of the KREEP-rich rocks in the Aristillus target materials. This is supported by  $\delta D$  data from relict apatite grains in the impact melt of 15405 (Barnes et al., 2014b) that have preserved low  $\delta D$  values similar to those measured in 15403 and 15404 in this study.

The presence of a very low D reservoir in the lunar interior has interesting implications for potentially degassed samples with low  $\delta D$  values ( $\approx -100$  ‰), such as the two basalts (NWA 773 and 14053) that have  $\delta D$  signatures in the terrestrial range. Both of these samples have had their low  $\delta D$  values explained by lack of degassing (NWA 773, average  $\delta D \approx -29$  ‰, Tartèse et al., 2014) or incorporation of low D solar wind during impact heating (14053, average  $\delta D \approx -190$  ‰, Greenwood et al., 2011). However, if a very low D reservoir existed in the Moon perhaps these samples owe their low  $\delta D$  signatures to a mantle source that was depleted in D. We calculate that if they had started with  $\delta D$  value of  $-500$  ‰, similar to the average  $\delta D$  value of 15404,55, the average  $\delta D$  values of apatite in both 14053 and NWA 773 could be obtained with

> 85 % H<sub>2</sub> loss. This did not necessarily occur for these samples, but it is an intriguing possibility.

## 5.2 Heterogeneous water distribution in the lunar interior?

The low H<sub>2</sub>O content (< 500 ppm) measured in the majority of KREEP-related materials is in stark contrast to the higher H<sub>2</sub>O contents (~1000-7500 ppm) of apatites in most mare basalts (Figs. 3, 4). Important exceptions are norites 77215 and 78235, and a granite clast in 14303 (Barnes et al., 2014a). Despite attempts to calculate magmatic water contents from apatite data (McCubbin et al., 2010, Boyce et al., 2010, Barnes et al., 2013, Tartèse et al. 2013, 2014, Robinson et al., 2013), Boyce et al. (2014) have shown that partitioning of OH, F, and Cl into apatite is complicated and depends on the relative and total abundances of these species, the timing of apatite crystallization, and the extent to which equilibrium was maintained during apatite crystallization of the melt. Estimating water content is further complicated by formation of late-stage melt pockets during crystallization in a lava flow (Pernet-Fisher et al., 2014).

While estimating the water content of a magma from apatite H<sub>2</sub>O might not be possible, the H<sub>2</sub>O concentration of residual glass in KREEP basalts in rock 15358 can be used to estimate the initial concentration in the magma before crystallization and loss occurred. The glass contains between 58 and 95 ppm H<sub>2</sub>O (Table 1) and represents the last ~20 % of melt remaining, as determined by modal analyses (Taylor et al., 2012). Because water is incompatible in all lunar minerals except apatite, its initial concentration in the magma would have increased as plagioclase and pyroxene crystallized. Thus, if no loss of H<sub>2</sub>O occurred, the parent magma would have contained 20% of the amount we measured in the glass, 12–19 ppm H<sub>2</sub>O. The relatively high  $\delta D$  value (average of +560 ‰, corrected for spallation) of the glass suggests that the magma might have lost water, as expected for a lava flow. To assess the initial water content, we calculated the amount of water loss by assuming that the initial  $\delta D$  value was -100 (earthlike) that loss was dominated by H<sub>2</sub>, and that the final  $\delta D$  is what we observe in the KREEP basalt clasts (+560 ‰), following the method used by Tartèse et al. (2013). The results are shown in Fig. 5. An initial  $\delta D$  value of -100 ‰ requires an initial H<sub>2</sub>O concentration of

115 ppm to produce the mean  $\delta D$  value of +560 ‰ and 85% loss of initial H. A lower initial  $\delta D$  value would require a higher initial water content, but also a greater loss of H. Initial  $\delta D$  equivalent to VSMOW implies an initial  $H_2O$  content of 80 ppm, requiring 80 % loss of the initial water to obtain a  $\delta D$  of 560 ‰. An initial  $\delta D$  signature of -500 ‰ (at the top of the range for the Apollo 15 QMDs), requires > 99.9 % water loss, which is unreasonable considering that the pyroclastic glasses lost only about 98% (Saal et al., 2008).

These estimates lead us to conclude that the lava in which the KREEP basalt clasts in 15358 formed could have had an Earth-like initial  $\delta D$  signature ( $\sim 0$  ‰) and  $\sim 100$  ppm  $H_2O$ . For comparison, melt inclusions in olivine in Apollo 17 orange glass beads (Hauri et al., 2011; Saal et al., 2013) contain 270–1200 ppm. Assuming that lower values reflect H loss from the inclusions, we infer that the orange glass magma contained  $\sim 1000$  ppm  $H_2O$ , about an order of magnitude larger than we estimate for the KREEP basalts in 15358. Saal et al. (2008) calculated from diffusion profiles of H, Cl, F, and S that the pre-eruption magma for the VLT glass contained 260–745 ppm  $H_2O$ , consistent with melt inclusion measurements in the orange glass. Assuming 10% partial melting, the mantle sources for the orange glass, green glass, and KREEP basalt magmas would have contained 100 ppm, 75 ppm, and 10 ppm  $H_2O$ , respectively, suggesting a range in mantle  $H_2O$  contents. Clearly, more work on KREEP basalts and KREEP-rich glasses is needed in order to fully understand the relationship between glass/melt inclusion  $H_2O$  content and source region water content.

### ***5.3 Implications for the lunar interior.***

The primary goal of all measurements of water in volcanic glasses, melt inclusions, and apatites is to determine the bulk water content and sources of water in the Moon. The observed heterogeneities in water abundance and  $\delta D$  values in the lunar interior present a major problem, as it is unclear which samples, if any, are the most representative of the Moon as a whole. The most reliable  $H_2O$  abundance measurements for determining pre-eruptive water content of lunar magmas come from the melt inclusions in olivine in pyroclastic glass



beads, which indicates that at least one part of the lunar interior contains as much water as the source regions of MORBs (Hauri et al., 2011). These melt inclusions did not lose much water when they formed, which means their  $\delta D$  values are minimally fractionated (Saal et al., 2013). After correction for spallation, the  $\delta D$  values of the A17 melt inclusions range from +187 to +327 ‰ (Saal et al., 2013). To the extent that H loss did happen, the original  $\delta D$  would have been lower. This is near the Earth range, but it is also near the range of the moderately-enriched  $\delta D$  value reservoir discussed above, which primarily consists of KREEP-rich, intrusive rocks. This may also indicate that the moderately enriched reservoir could be related to the Earthlike reservoir.

Füri et al., (2014) reported data suggesting that the source of the Apollo 17 orange glass (74002) had an initial  $\delta D$  value of  $-100$  ‰, which is within the range of the terrestrial mantle. Does this suggest a common source of water in the terrestrial mantle and some portions of the lunar interior? Füri et al., (2014) point out that a  $\delta D$  value of  $-100$  ‰ is within the range of carbonaceous chondrites, and could indicate the delivery of at least some water to the Earth-Moon system by late accretion (e.g., Saal et al., 2013; Tartèse and Anand 2013; Tartèse et al., 2013; Tartèse et al., 2014). However, if this water was not added after lunar formation to the Earth-Moon system, then it could be conceived that water was retained during the Giant Impact event allowing for some regions to contain substantial water, with Earth-like  $\delta D$  signature (Saal et al., 2013; Barnes et al., 2014a; Füri et al., 2014).

Greenwood et al. (2011) were the first to measure  $\delta D$  signatures of apatite in lunar samples, and they showed that apatite in mare basalts were characterized by elevated  $\delta D$  values ( $> 800$  ‰). They suggested that the Moon accreted dry (constrained by Moon-formation-evolution models available at the time), and water was added later from a source, such as comets, already characterized by water with high  $\delta D$  values. This seems unlikely. The mare basalts almost certainly lost water when erupted, so their  $\delta D$  values are elevated by the process of magmatic degassing of  $H_2$  which preferentially fractionates H over D isotopes (as discussed in the previous sections). Tartèse and Anand (2013) calculated that pre-eruptive mare basalt magmas could have been characterized by  $\delta D$  values of  $\sim 100$  ‰, but lost 85-99 % of their



water, which consequently elevated the  $\delta D$  value of the water. Thus, there is no compelling need for a source with high  $\delta D$  values in the lunar interior. It is possible that late-delivered volatiles could have been added after the mantle cumulates were formed but prior to the formation of a significantly thick crust (e.g., Hauri et al., 2015).

The apparently dry regions of the lunar interior vary in  $\delta D$  values from moderately enriched to extremely depleted. The regions that are moderately enriched compared to Earth may reflect fractionation in the proto-lunar disk after the Moon-forming impact (Desch and Taylor, 2012; Hauri et al., 2015). Fractionation of D from H (preferential loss of lighter H) is consistent with the presence of heavy Zn isotopic signatures in lunar samples (Paniello et al., 2012). H loss from the disk needs to be modelled thoroughly, but if H loss was high ( $\sim 90\%$ ) during lunar formation, D/H fractionation could have been sufficient to change the  $\delta D$  value from  $-218\text{‰}$  (the lower range of terrestrial mantle values) to the range shown by the moderately enriched lunar reservoir ( $+200$  to  $+400\text{‰}$ ). Alternatively, the potentially dry regions of the lunar interior with  $\delta D$  values in the terrestrial range might reflect Moon-forming materials that lost water, but did not fractionate D from H. The regions with Earth-like  $\delta D$  signatures could also have formed by extensive fractionation of H from D during lunar formation, but began with a low  $\delta D$  values like those observed in Apollo 15 QMD apatites. This implies that the primitive Earth could have had a much lower  $\delta D$  signature than is currently considered for the present-day upper mantle. In fact, primitive mantle sources have been identified and at least some contain low  $\delta D$  values, as low as  $-218 \pm 34\text{‰}$  (Hallis et al., 2015). Halliday (2013) explains the Earth's low  $\delta D$  as a mixture of chondritic and solar components.

Our study has contributed to the growing dataset for water and H-isotopes from lunar apatites, and has targeted mostly intrusive rocks of the lunar highlands (felsites and QMDs). The data presented are in agreement with previous work advocating for the heterogeneous distribution of water in the lunar interior (e.g., Anand, 2010; McCubbin et al., 2011; Robinson and Taylor, 2014). The apatites in Apollo 15 QMDs record a water reservoir in the lunar interior that is characterized by an anomalously low D/H ratio ( $\sim -600\text{‰}$ ), the lowest yet recorded for the lunar interior. This is distinct from the majority of lunar samples, which range in  $\delta D$  values

of -200 to +100 ‰ compatible with results from lunar highlands cumulates, mare and KREEP basalts, and picritic glasses (Saal et al., 2013; Füre et al., 2014; Barnes et al., 2014a; Tartèse et al., 2014), though some samples have  $\delta D$  values as high as +600 to +700 ‰. The origin or source of this uniquely D-depleted reservoir is ambiguous but could be an isotopic signature resulting from Moon formation through fractionation of H isotopes in the protolunar disk, the incorporation of a primitive Solar component to the lunar interior, or a signature inherited from a depleted reservoir in the proto-Earth.

## Summary and Conclusions.

The measurements of KREEP-rich intrusive samples presented here, along with literature data, show that apatite in the KREEP-rich intrusive rocks is low in  $H_2O$ . Though apatite cannot be used to calculate pre-eruptive magmatic water content, our measurements of residual glass in KREEP basalt fragments in 15358 suggest that the KREEP-basaltic parent magmas to the felsites and QMDs was very dry, with the mantle source of 15358 containing  $\sim 10$  ppm  $H_2O$ , about ten times less than the mantle source of the A17 pyroclastic glasses. This suggests at least two different reservoirs for water in the lunar mantle; one “wet” and one “dry”, which complicates determining the bulk water content of the Moon.

In addition to the water content of apatite in these KREEP-rich intrusive rocks, we have also measured their H isotope compositions and compared them with literature data. Lunar apatites show an astonishingly large range in  $\delta D$  and may fall into a number of reservoirs. Many lunar rocks, including the mare basalts, seem to have had initial  $\delta D$  similar to that of Earth’s mantle, while the drier KREEP-rich rocks studied here are moderately elevated in D with respect to Earth. The most surprising results came from apatite in Apollo 15 QMDs 15404, 51, 15404,55, and 15403, 71, which have the lowest  $\delta D$  measured in lunar apatite so far, as low as -754 ‰. These QMDs may represent another reservoir in the lunar mantle that could preserve a primitive, D-depleted component within the Moon, perhaps inherited from the proto-Earth.

Our data indicate that water is heterogeneously distributed in the Moon, varying in both concentration and hydrogen isotopic composition. How these distinctive reservoirs formed is

unclear, but likely reflect a combination of lunar formation and differentiation. Bulk lunar water concentration is difficult to constrain, but the variability in water content and D/H may be much more informative about lunar origin than is the total amount of water in the Moon.

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967 **Table**

Sample		ppm H <sub>2</sub> O	ppm H <sub>2</sub> O 2 $\sigma$	$\delta D$ ‰	$\delta D$ 2 $\sigma$	Corrected $\delta D$ ‰	$\delta D$ 2 $\sigma$	detect. limit (ppm H <sub>2</sub> O)	Instrument
14305, 656	apt1	23	1	799	650	735	652	13	NanoSIMS
	apt3 #2	136	4	491	320	481	320	13	NanoSIMS
	apt3 #3	41	1	-28	528	-65	528	13	NanoSIMS
	apt3 #4	37	1	973	513	934	514	13	NanoSIMS
	apt4	49	2	-76	458	-107	459	13	NanoSIMS
	apt5	54	2	-6	481	-34	481	13	NanoSIMS
	apt6	36	1	649	417	608	418	13	NanoSIMS
	apt7	53	2	-139	420	-168	420	13	NanoSIMS
14321, 1047	apt1 #1	<100		n.d.		n.d.		100	ims-1280
	apt1 #2	<100		n.d.		n.d.		100	ims-1280
	apt1 #3	82	2	247	415	231	415	24	NanoSIMS
	apt2 #1	<24		n.d.		n.d.		24	NanoSIMS
	apt2 #2	137	3	-108	364	-118	364	24	NanoSIMS
	apt4	93	2	-313	439	-327	439	24	NanoSIMS
	apt5	<24		n.d.		n.d.		24	NanoSIMS
	apt6 #1	66	2	943	356	925	356	24	NanoSIMS
	apt6 #2	76	2	806	317	790	317	24	NanoSIMS
14161, 7069	trapt #1	162	49	231	55	114	66	110	ims-1280
	trapt #2	189	57	265	56	165	62	110	ims-1280
14161, 7373	apt3	174	52	432	56	323	70	110	ims-1280
	apt2	<110		n.d.		n.d.		110	ims-1280
	apt1	<110		n.d.		n.d.		110	ims-1280
15403,71	apt1 #1	77	9	-589	78	-597	79	6	ims-1280
	apt1 #2	181	20	-721	48	-724	48	6	ims-1280
	apt1 #3	129	14	-749	56	-754	57	6	ims-1280
15404,51	apt6 #1	58	6	-428	135	-438	138	6	ims-1280
	apt6 #2	46	6	-640	80	-653	82	6	ims-1280
15404, 55	apt1 #1	134	4	-587	432	-592	432	13	NanoSIMS
	apt1 #2	267	9	-344	319	-346	319	13	NanoSIMS
	apt2 #1	76	2	-344	492	-352	492	13	NanoSIMS
	apt2 #2	99	3	-683	491	-689	491	13	NanoSIMS
	apt2 #3	99	3	-541	491	-547	491	13	NanoSIMS
	apt2 #4	69	2	-505	523	-514	523	13	NanoSIMS
15358,6	gls c4 #1	95	11	698	71	566*	88	10	ims-1280
	gls c4 #2	95	11	610	71	477*	86	10	ims-1280
	gls c1 #1	58	7	789	84	572*	124	10	ims-1280
	gls c1 #2	64	8	830	83	634*	117	10	ims-1280
76535, 52	apt1	75	7	791	66	639	93	22	ims-1280
76535,56	bigapt #1	62	6	572	79	388	106	22	ims-1280
	bigapt#2	86	8	475	110	342	103	22	ims-1280
	bigapt #3	<22		n.d.		n.d.		22	ims-1280
77538,16	apt1	175	55	335	74	304*	74	100	ims-1280
	apt2	188	55	411	74	383*	74	100	ims-1280

Table 1. Measured H<sub>2</sub>O abundances and  $\delta$ D values of lunar apatites and glasses\*. Multiple measurements on the same grain are indicated by a #. Italic font denotes measurements below our detection limit. *n.d.* - not detected. Analytical errors are  $2\sigma$ . Corrected  $\delta$ D values are those after correcting for the contribution of spallation-produced D, and uncertainty on the corrected  $\delta$ D values is dominated by large uncertainty in the D production rate.

\*Exposure ages have not been determined for these samples. The CRE age estimates used here are described in section 3.2.

## Figure Captions

Fig. 1. Representative backscattered electron (BSE) images of samples described in this work. Where visible, apatites are denoted by arrows. (a) Graphic intergrowth of quartz (dark gray) and K-feldspar (light gray) in 14321, 1047. (b) Felsite-ferrobasalt silicate liquid immiscibility pair in 77538, 16. The darker intergrowth is quartz and K-feldspar, while the bright areas are Fe-rich olivine, pyroxene, and amorphous silica. Fe-Ni metal and ilmenite are also present. (c) Portion of quartz monzogabbro 15404, 55. (d) Portion of quartz monzodiorite 14161, 7373. The exsolved phase is inverted pigeonite, while the brightest phase is merrillite (Jolliff et al. 1999). The bleb near the center of the image is intergrown silica and K-feldspar formed through immiscibility. Bright squares are ion microprobe analysis pits. (e) Apatite-merrillite intergrowth surrounded by plagioclase in troctolite 76535 56. The darkest phase is olivine. Round dark marks in the apatite are pits from previous analyses. Note the large grain size. (f) Apatite-merrillite intergrowth in an alkali anorthosite clast in breccia 14305, 656. The bright gray is merrillite, the darker intergrowths are apatite (indicated by arrow). Darkest gray is plagioclase.

Fig. 2. Sample calibration curves for ims-1280 analysis. (a)  $^1\text{H}/^{18}\text{O}$  calibration curve for  $\text{H}_2\text{O}$  in apatite and (b)  $^1\text{H}/^{30}\text{Si}$  calibration curve for  $\text{H}_2\text{O}$  in basaltic glass. Similar calibration curves were used to calibrate NanoSIMS data.

Fig. 3. Apatite data for KREEP-rich intrusive samples, with  $2\sigma$  error bars. The spallation correction can lower the  $\delta\text{D}$  of apatite by  $> 100\%$  in samples with long cosmic ray exposure ages.

Fig. 4. Plot showing  $\delta\text{D}$  value versus ppm  $\text{H}_2\text{O}$  content of apatite in this study (colored points) compared with literature apatite data (grayscale points, Greenwood et al. 2011; Tartèse et al. 2013, 2014, Barnes et al. 2013, 2014a). Note the log scale on the x-axis.

1004

1005 Fig. 5(a)(b) BSE images of KREEP basalt fragments containing quenched residual glass in  
1006 15358,6. Dark, straight-sided phase is plagioclase, medium gray is pyroxene, and the bright  
1007 areas are Fe-rich yellow glass. Silica (darkest gray) and ilmenite (white needles) are also  
1008 present. White squares indicate ion microprobe analysis pits. (c) Calculation of the increase in  
1009  $\delta D$  value due to hydrogen loss, constrained by the  $\delta D$  value measured in 15358 KREEP basalt  
1010 glass (corrected for crystallization). To reach the observed  $\delta D$  in 15358 requires loss of 85% of  
1011 an initial  $H_2O$  concentration of 115 ppm.

1012

1013 Fig. 6. Histogram of the lowest apatite  $\delta D$  measurement in lunar samples by rock type,  
1014 including literature data from Greenwood et al. (2011); Tartèse et al. (2013, 2014), and Barnes  
1015 et al. (2013, 2014a). The lowest  $\delta D$  apatite should represent the  $\delta D$  value least affected by  
1016 degassing, if degassing occurred. The range in  $\delta D$  value of Earth's mantle and CI and CM  
1017 chondrites is also shown (Boettcher et al., 1980; Michael 1998; Ahrens 1989; Deloule et al.,  
1018 1991; Bell and Rossman 1992; Thompson 1992; Graham et al., 1994; Jambon 1994; Wagner et  
1019 al., 1996; Xia et al., 2002; Alexander et al., 2012; Hallis et al., 2015). The protosolar  $\delta D$  value of  
1020  $\sim -865 \pm 32$  ‰ is from Geiss and Gloecker (1998). There appear to be at least three H reservoirs  
1021 in the lunar interior: an Earth-like reservoir, a moderately elevated reservoir, and a very low D  
1022 reservoir. The mare basalts would have had an initial undegassed  $\delta D$  signature compatible with  
1023 the Earth range,  $\sim 100$ ‰ (Tartèse and Anand 2013).

1024



Figure 1

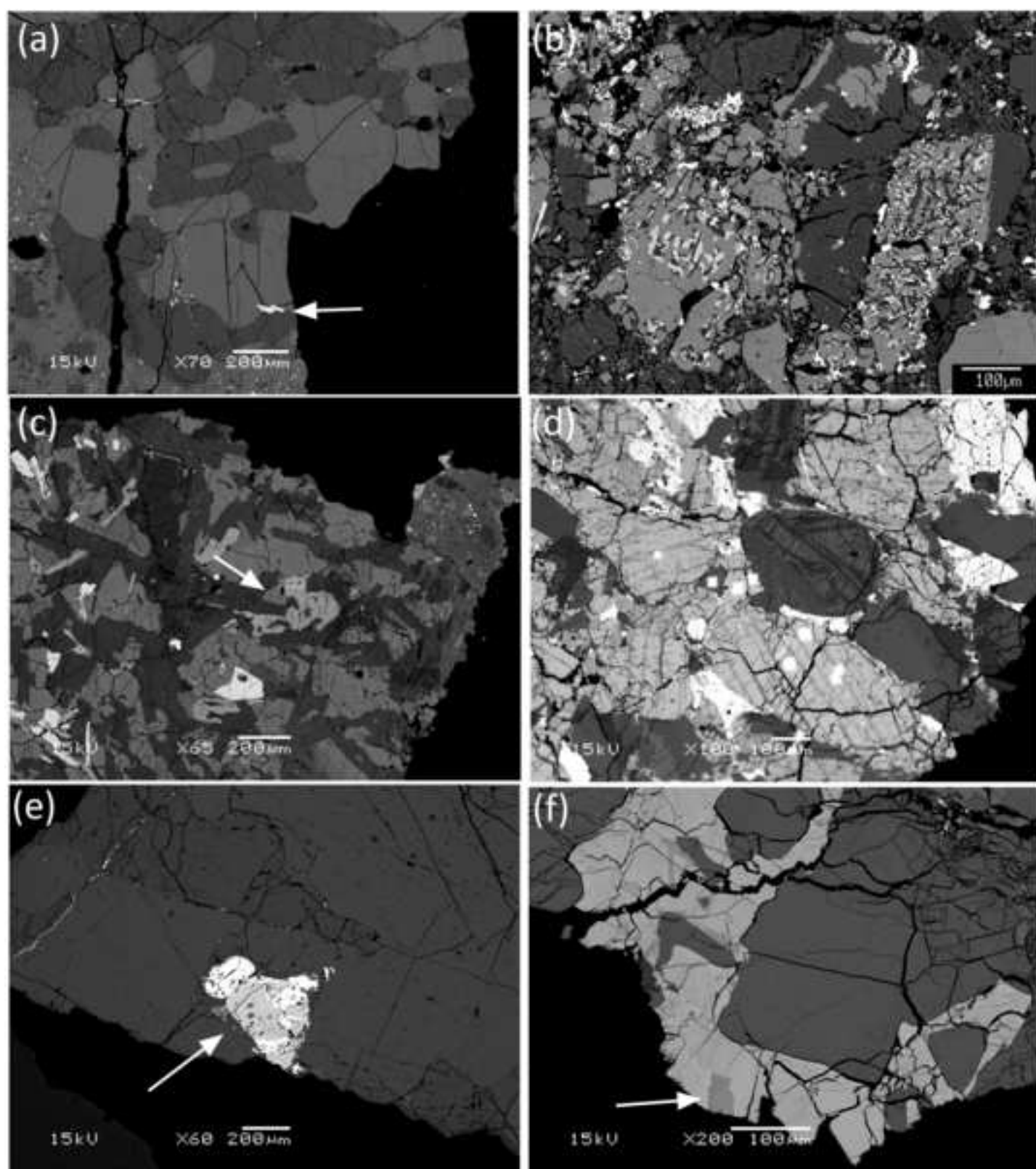


Figure 2

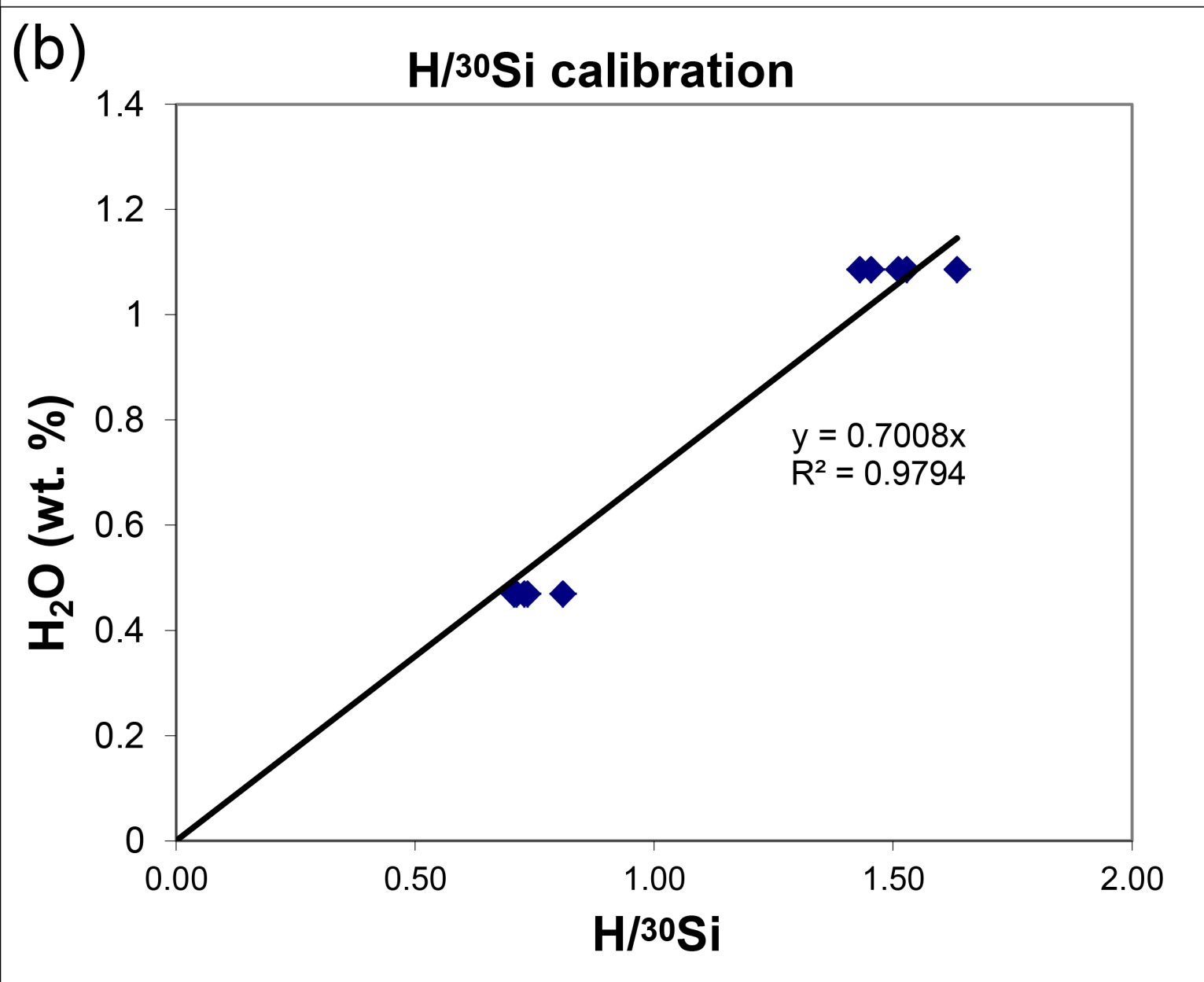
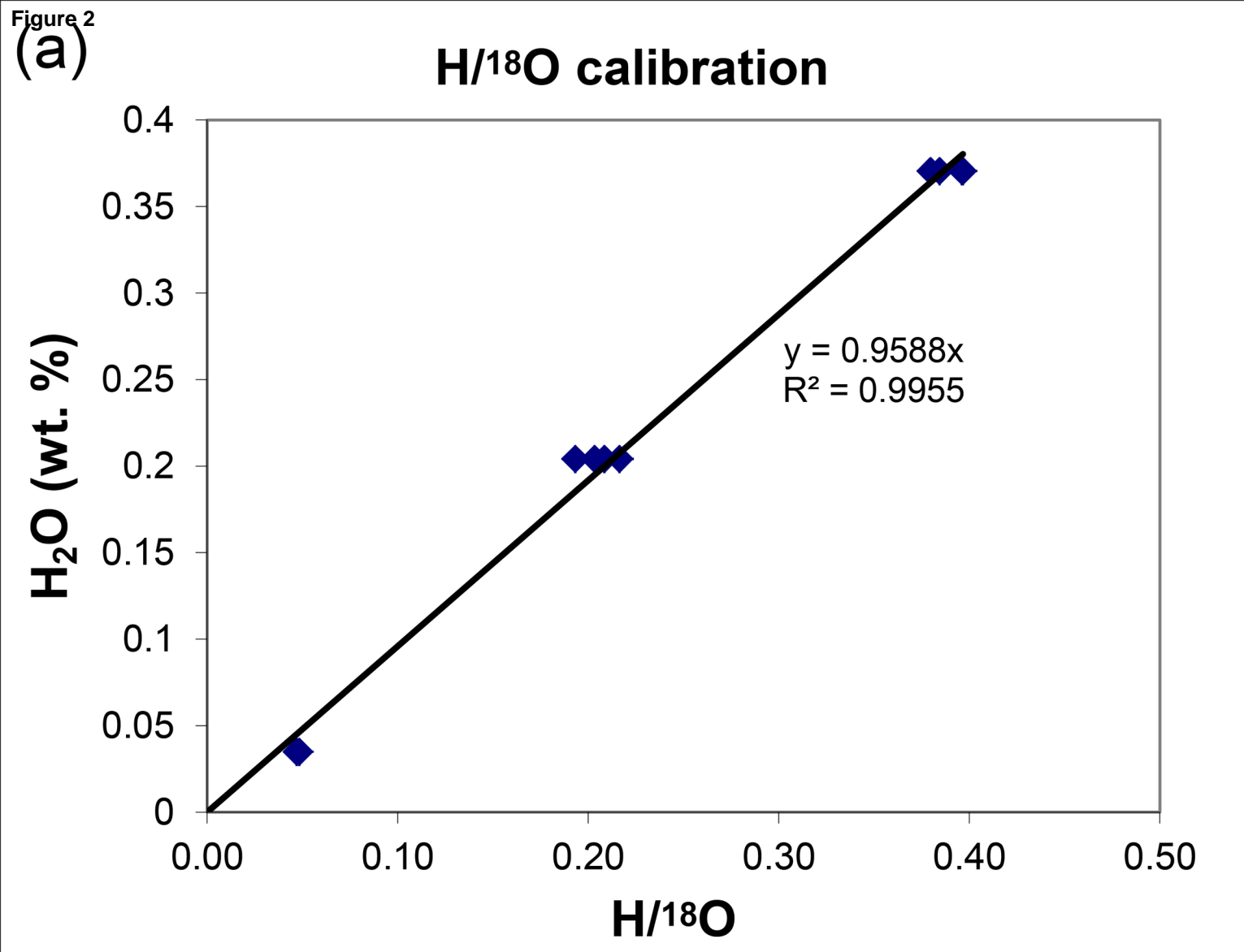


Figure 3

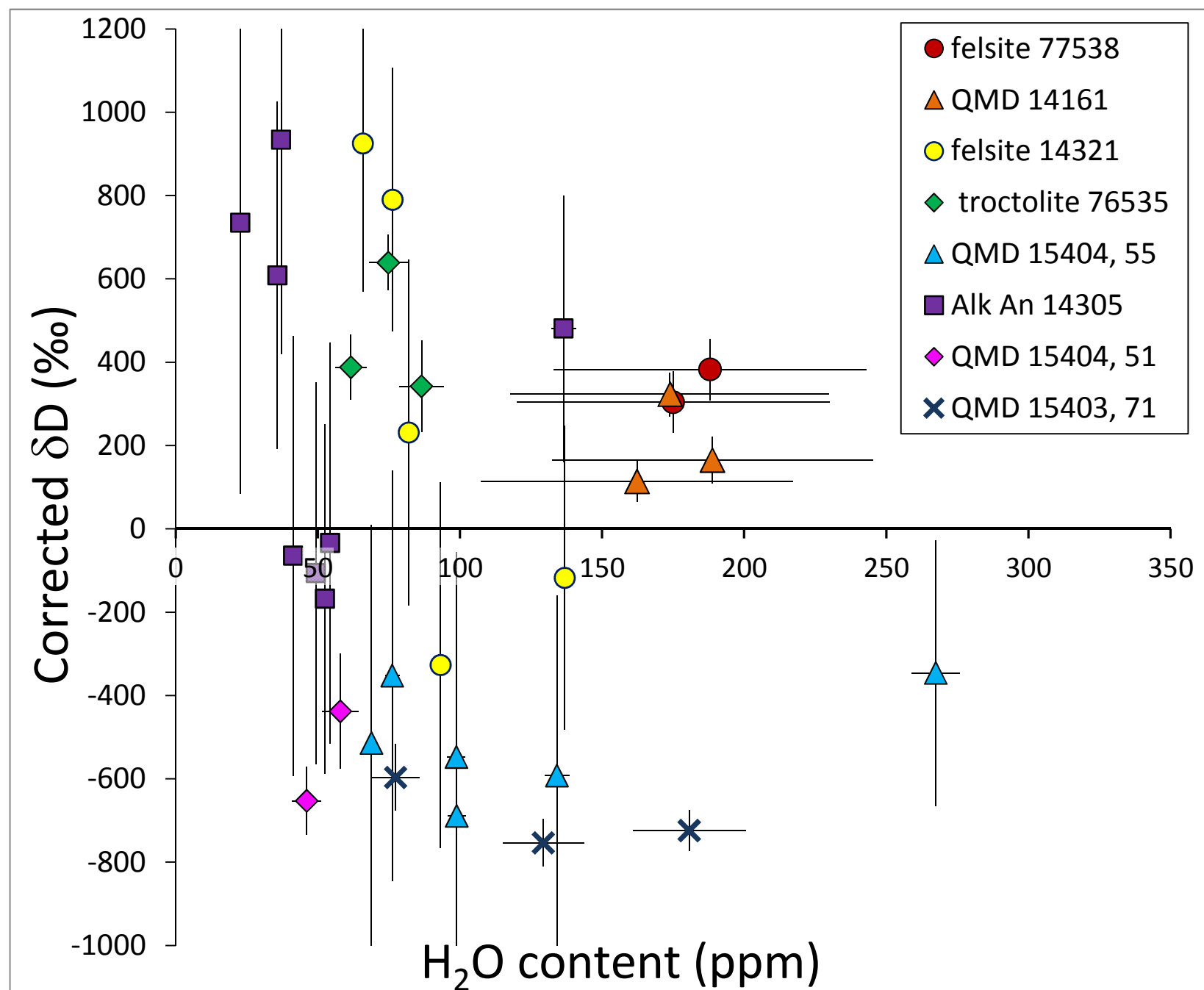
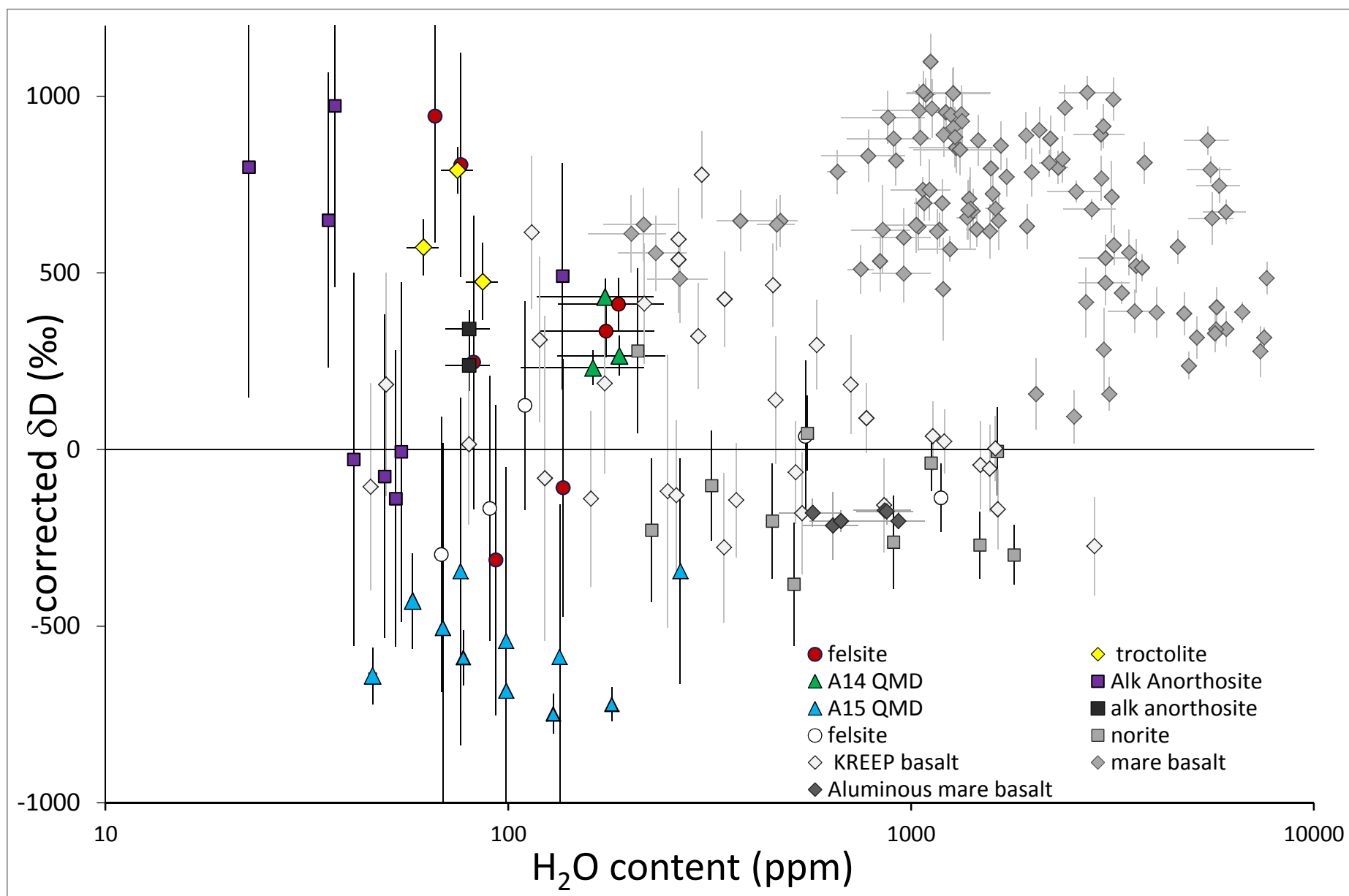
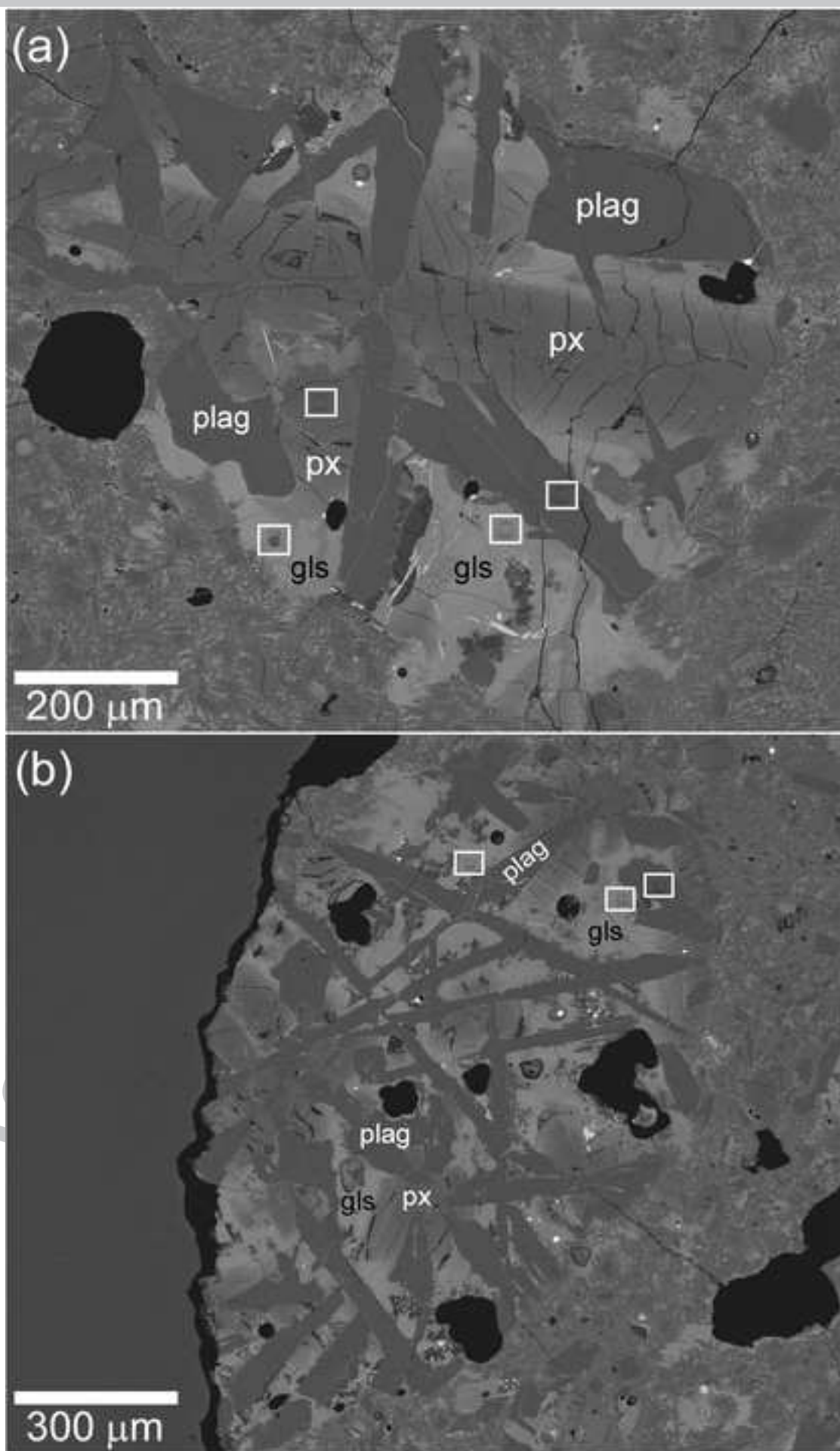


Figure 4





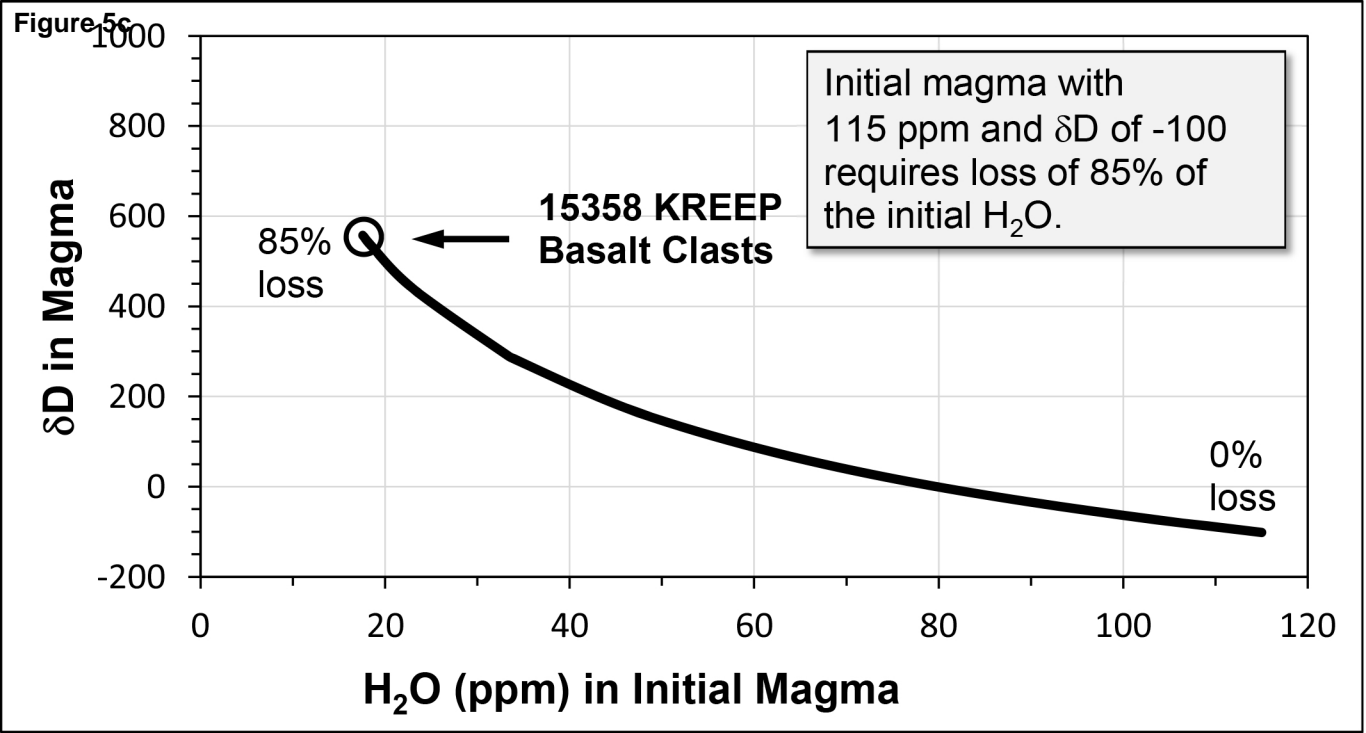


Figure 6

